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THIRD INTERNATIONAL SYMPOSIUM ON SOLUBILITY PHENOMENA

23 – 26 August 1988

University of Surrey
Guildford, Surrey
England

ABSTRACTS

Sponsored by

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

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This Symposium is dedicated to the memory of

PROFESSOR STEVEN KERTES

Chief Editor of the Solubility Data Series who died unexpectedly on 11 July 1988.

Professor Kertes played a vital role in the development of the work of the Solubility Commission and will be greatly missed by all his colleagues.

THIRD INTERNATIONAL SYMPOSIUM ON SOLUBILITY PHENOMENA (3RD ISSP)

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SCIENTIFIC PROGRAMME

Tuesday morning, 23 August 1988

08 30 – 09 00	Opening of the Symposium by Dr Angela F Danil de Namor, Co–Chairman of the Symposium
	Welcome by Professor J D E Beynon, Pro Vice Chancellor, University of Surrey
	Welcome by Professor I Wadsö on behalf of the International Union of Pure and Applied Chemistry
	Welcome by Professor J W Lorimer on behalf of the Solubility Commission

SESSION 1

Microcalorimetry and Solubility Studies; Models For Studies of Solution

Co–Chairmen: J W Lorimer (Canada): V M Valyashko (USSR)

09 00 – 09 45 PLENARY LECTURE: Micro Solution Calorimetry
I Wadsö, University of Lund, Sweden

10 00 – 10 20 Correlation of Solubility Data in Ternary Liquid Mixtures
C McDermott and Y Demirel, Engineering Department
University of Birmingham, UK and Faculty of Art and Sciences,
Cukurova University, Adana, Turkey

An empirical correlation may be very helpful for practical calculations and interpolations of ternary solubility data. It is also needed in predicting the phase splitting of a ternary liquid mixture for vapour–liquid–liquid equilibria calculations.[1] Such a correlation has been suggested by Hlavaty.[2] The correlation is applicable for ternary type I mixtures. It also requires that the slopes at points of intersections with horizontal axis must have opposite signs which is not the case for some of the solubility data.

In this study, a general quadratic equation with five constants is used to correlate a binodal curve of a ternary mixture with one or two partially miscible pair. It imposes no restriction on the solubility data to be used. The predictions of solubility data by the equation has been compared for 27 ternary systems.

References

1 Y Demirel and C McDermott, Chim Acta Turc, 1984, 12, 173

2 K Hlavaty, Coll Czech Chem Commum, 1972, 37, 4005

10 40 – 11 00 Application of Computer Molecular Modeling to the Estimation of Water Solubility of Organic Compounds

D C Roberts, MITRE Corporation, 7525 Colshire Drive, McLean, Virginia 22102, USA

Most available methods for estimating water solubility of organic compounds employ the "additive–constitutive" principle, in which numerical values representing structural fragments or features present in the molecule, are added together to arrive at an estimated solubility value. This methodology works well for relatively simple compounds containing standard functional groups, but works poorly or not at all when unusual functional groups or structural features are present, or when the molecule is highly functionalized. Unfortunately, it is often in just such situations that a water solubility estimate is needed.

The recent availablity of sophisticated molecular modeling software has made it possible to adopt a holistic approach to the estimation of water solubility. In this approach, we begin with a large set of diverse compounds having reliable water solubility values. Molecular modeling software is employed to generate a representative three–dimensional structure for each compound. This serves as the basis for computation of a set of information–rich scalar values (descriptors) for each compound. Water solubility is correlated with the descriptors for the full set of compounds; the correlation equation may then be used as an estimation function. The statistical techniques used to derive and validate this equation, and the choice of descriptors used, are critical elements of this approach.

11 10 – 11 30 Extensions of the One–Parameter Group Contribution Model for Liquid Mixtures

D Knox and S Rami, Department of Chemical Engineering, Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, New Jersey, USA

The group–contribution model for activity coefficients[1] previously presented has been extended 1) to cover additional functional groups, and 2) to cover additional properties such as heats–of–mixing.

This paper discusses some of the results which have been obtained when using this model for the prediction of both activity coefficients and heats–of–mixing. Comparative results with other predictive methods are given.

References

1 D E Knox, J Soln Chem, 1987, 18, 625

11 40 – 12 00 Can We Predict Which Solids Exist in Equilibrium With Saturated Ternary Solutions?

R Duhlev, I Brown and C Balarew*
Institute for Materials Research, McMaster University,
Hamilton, Ontario, Canada, L8S 4MI
*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria

More than 40 double salts of the type $xMeX_2.yMe'X_2.zH_2O$ have been reported to exist in equilibrium with the saturated solution in ternary MeX_2–$Me'X_2$–H_2O systems (X = Cl or Br; Me and Me' = Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn, Cd).[1] The double salts show a variety of compositions but over 80% of them belong to 4 particular types. The possible compositions and structures of double salts are considered in the light of two models: the hard and soft acid–base concept[2] and the bond valence model.[3] A basic consideration in our approach is the assumption that ions found in the solid will either already exist in the saturated solution in sufficient concentration or will be directly derivable from ions in the solution (eg by condensation with the elimination of water). A few simple assumptions, such as the good match between the acid–base strengths of the complex cation and the complex anion, can explain why the composition $2MeX_2.Me'X_2.12H_20$, $MeX_2.Me'X_2.8H_20$, $MeX_2.Me'X_2.6H_20$ and $MeX_2.2MeX_2.6H_20$ are favoured.

References

1 R Duhlev and C Balarew Z Anorg Allg Chem, 1987, 549,225

2 C Balarew and R Duhlev J Solid State Chem, 1984, 55, 1

3 I D Brown in "Structure and Bonding in Crystals", Vol II, Eds, M O'Keefe and A Navrotsky, Academic Press, 1981, pp 1–30

12 10 – 12 30 Modelization of Solid–Liquid Equilibria in the Systems H_2O –M_2HPO_4 (M = Na,K)

R Tenu, A Hammami, J J Counioux,
Laboratoire de Physico–Chimie minerale II,
UA CNRS 116 43, Université Claude Benard–Lyon 1
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The phase equilibria of the binary systems H_2O–Na_2HPO_4 and H_2O–K_2HPO_4 were experimentally studied up to 120°C. In this range of temperature, five hydrates present stable equilibria with the saturated solution: $Na_2HPO_4.12H_2O$, $Na_2HPO_4.7H_2O$, $Na_2HPO_4.2H_2O$, $K_2HPO_4.6H_2O$ and $K_2HPO_4.3H_2O$.

In a first time, complementary solubility determinations were carried out below 25°C by conductivity measurement.[1] By using a method previously described [2-5] the solubility data were then analysed and the results show the existence of two phenomena in the solution:

- a partial dissociation of the alkali hydrogenophosphates which is confirmed by conductimetry
- a solvation of the ionic species. The hydration numbers obtained are in good agreement with the bibliography values

Finally, the modelization of the solid–liquid equilibria allows an excellent representation of the liquids curves. Furthermore, the heat of fusion of each hydrat was calculated and the obtained values are very close to those obtained by differential scanning calorimetry.

References

1 J Berthet, R Tenu, J J Counioux, Thermochimica Acta, 1983, 68, 145

2 J J Counioux, R Tenu, J Chim Phys, 1981, 78(10), 815

3 R Tenu, J J Counioux, J Chim Phys, 1981, 78(10), 823

4 R Tenu, J J Counioux, R Cohen–Adad, Eight International Codata Conference Warsaw), 1983

5 J J Counioux, R Tenu, J Chim Phys, 1985, 82(1), 43

12 40 – 13 00 Solubility of Metals in Low Melting Metals

C Guminski, Department of Chemistry, University of Warsaw,
Pasteura 1, 02093 Warszawa, Poland

Knowledge on metallic solubilities is, first of all, important for metallurgy, electrochemistry, nuclear and space technology.

Experimental solubilities of metals in liquid Hg, Ga, In, Pb, Bi and alkali metals were collected, evaluated and selected. Prediction models for the solubilities were outlined. A comparison between the experimental and the predicted values was carried out.

Taking into account the solubility of metals in mercury and their tendency to formation of intermetallics, a classification of the simple amalgams into 4 groups is proposed. The classification is reflected in the corresponding phase diagrams, heat of dissolution processes, activity and diffusion coefficient of metals in mercury as well as kinetics of electroreduction of metallic aquocations on a mercury cathode.

Tuesday afternoon, 23 August 1988

SESSION 2

Solubility of pollutants an other Inorganic Substances

Co–Chairmen: R.P. Tomkins (USA); A. Szafranski (Poland)

14 00 – 14 45 PLENARY LECTURE: Solubility and Pollution of Radio–nuclides

J D Wilkins, UK Atomic Energy Authority, Harwell, (UK)

15 00 – 15 20 Estimation of the Importance of Air Stripping in the Biological Treatment of Various Priority Pollutants

D E Knox and G A Lewandowski,
Department of Chemical Engineering, Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, New Jersey, USA

In general, the possiblity that pollutants are being air–stripped is a subject of concern with hazardous waste treatment facilities which employ aerobic biodegradation.

There are often insufficient data available in order to be able to accurately judge whether a particular pollutant is likely to be a problem in a given facility. This insufficiency, however, can often be overcome through the application of predictive models for solubility.

This paper focuses on the prediction of stripping rates for several priority pollutants and considers the general implications of these rates in the biodegradation of hazardous wastes.

15 30 – 15 50

Mutual Solubilities of Hydrocarbons and Water at Ambient and High Temperatures

H H Hooper, S Michel, J M Prausnitz
Department of Chemical Engineering, University of California, Berkeley, USA

Mutual solubilities of hydrocarbons and water are important for design and operation of process equipment for petroleum refineries, coal processing plants, and water–purification steps. Temperatures encountered in water–hydrocarbon contacting processes range from ambient to well above 200°C. Experimental mutual solubility data are abundant at temperatures close to ambient: however, high–temperature data are limited. This work presents mutual solubilities of two binary and two ternary aqueous systems in the range 75–200°C. Hydrocarbons studied include toxic pollutants (eg 1,2–dichloroethane, phenol, chlorobenzene) and aromatic derivatives commonly encountered in processing of fossil fuels (eg pyridine, thiophene, toluene). A group–contribution model of the UNIFAC type is used to correlate mutual solubilities for several classes of hydrocarbon derivatives over a wide temperature range. Predictions of ternary LLE based on binary group–interaction parameters are in fair agreement with experiment. The new correlation is useful for providing estimates of multicomponent water–hydrocarbon LLE in the range 20–250°C.

16 10 – 16 30 Treatment of Solubility Data of Aqueous Systems

V M Valyashko, N S Kurnakov, Institute of General and Inorganic Chemistry, Academy of Sciences of the USSR, Moscow 117907, Leninsky pr. 31

Obtaining the recommended values of solubility for so–called "easily soluble" substances (such as NaCl, NaOH etc) in aqueous systems includes both critical expert analysis and statistical processing of numerical data.

All published solubility data for equilibrium liquid – vapour – solid (for every system) were collected and subjected to examination. Fundamental assumptions were used in procedures of solubility data treatment:

solubility of each solid phase within a temperature range of stability is a smooth and continuous function of temperature

hypothesis on the proximity of the true values of solubility to the mean values of experimental data is assumed

tolerances of solubility data are dependent on the temperature range of measurements, experimental procedures and volume of information

The tolerances were estimated both from analysis of standard deviation values for the approximation arrays and from experience in the errors of experimental measurements. Some points were excluded from the data array if they display significant deviation from the mean values. The most reliable data are the averaged parameters of such singular points as melting, eutectic, peritectic.

Theoretical equations for temperature dependence of salt solubility are not available. Therefore, the averaging was carried out by expressing the dependences of concentration of saturated solution by an equation of the form $C = a + bT + cT^2 + ... + nT^m$, where C was the concentration, T was the temperature. Coefficients "a" to "n" were calculated on a computer using the least squares technique.

Attempts to assign statistical weights to solubility data were not satisfactory due to the lack of information about the experimental data in most of the papers examined.

16 40 – 17 00 Solubility Phenomena Investigation at Charles University, Prague, during the period 1968–1988

J Eysseltová, M Ebert, P Vojtíšek
Faculty of Science, Charles University, Albertov 2030
12840, Prague, Czechoslovakia

At the Department of Inorganic Chemistry of the Faculty of Science, Charles University, Prague, Czecholslovakia the mutual connection between composition and the properties of the phase complex has been emphasized in discussion of solubility diagrams. This approach, which attempts to cover all aspects of phase equilibria, corresponds to the correlation principle of classical physico–chemical analysis.

On the basis of the general diagram composition - property, some experimental modifications of the procedures used in the respective area were developed. An original method for the calculation of solubility curves based on the interaction constants characterizing every physico–chemical process taking place in the system under consideration has been derived. Based on this method, some attempts have been made to characterize the ionic processes in electrolyte solutions with the aid of solubility in ternary systems. Besides, some difficulties were found to explain the phenomena connected probably with the nature of concentrated electrolyte solutions.

17 10 – 17 30 Solubility Isotherms of Cu (II) Carboxylates in Pyridine – Water/ Organic Solvent Mixtures

I Uruska and I Stefańczyk, Department of Physical Chemistry, Technical University of Gdańsk, Gdańsk, Poland

Solubility isotherms have been measured for $Cu(O_2CR)_2$ – pyridine – water organic solvent ternary mixtures ($R = C_nH_{2n+2}$). The solubility (s) of copper (II) carboxylates has been found to strongly depend on the mixed–solvent composition, the kind of the co–solvent and the electronic and steric properties of the co–ordinating ligands (eg the ratios of solubilities of $Cu(O_2CCH_3)_2$ and $Cu(O_2CCH_2CH_3)_2$ in pure pyridine and in water are ≃ 10 and 1 respectively). For solutions equilibrated with solid mononuclear Cu (II) complexes the solubility is also strongly influenced by temperature; however the ln s vs. 1/T dependence deviates from linearity even within comparatively narrow temperature intervals. The results are compared with previous data from this laboratory on similar systems and discussed in terms of equilibria between ionic and non–ionic Cu (II) complexes in the solutions and solute–solvent interactions. Where possible, activity coefficients of the mononuclear and binuclear non–ionic complexes have been calculated. For the same type of complexes, these monotonically decrease with increasing the solubility parameter of the co–solvent.

17 40 – 18 00 **The Solubility of Iron in Sodium, an Example of the Complex Nature of Solutions in Alkali Metals**

Hans Ulrich Borgstedt, Institut für Material und Festkörperforschung, Kernforschungszentrum Karlsruhe, P O Box 3640, D–7500 Karlsruhe 1, Germany

The solubility of iron in liquid sodium is of importance for the understanding and modelling of corrosion of iron–based materials in the molten metal. Several solubility measurements have been performed so far. The results were scattered over three orders of magnitude, and even the values of the enthalpy of solution showed significant differences.

The most recent attempts to measure the solubility of iron in sodium also included an intensive pre–purification of the solute in order to reduce its oxygen content. Solubility measurements of iron in sodium gettered by uranium were applied to determine a relationship and the free enthalpy

$$\log c_{sat}^{Fe} \text{ (wt–ppm)} = 4.720 - 4116/T \text{ (K)}$$

of solution was ΔH_{sol} = 78700 J/g–atom. These results were in fair agreement with analyses of sodium samples taken from loops, in which the purification was performed by means of a cold trap. It seems that iron is the solid phase in equilibrium with the saturated solution.

Several other determinations of the solubility of iron in sodium were performed without special purification. At temperatures below about 600°C even low concentrations of oxygen in the range of 5 – 25 wt–ppm had influence on the saturation curves. These curves had all the same slope which could be expressed as ΔH_{sol} = 16100 J/g–atom, the constants of the equations were obviously dependent on the oxygen concentrations. The solid phase might not be metallic iron in these cases, though the ferrate Na_4FeO_3 is not existent at such low oxygen potentials.

Wednesday morning 24 August 1988

SESSION 3

Thermodynamics and Solubility studies

Co–Chairmen: F W Getzen (USA); A E Mather (Canada)

08 30 – 09 15 PLENARY LECTURE: The Thermodynamics of Solution
D Feakins, University College, Ireland

09 30 – 09 50 Standard Free Energies of Transfer of Some Haptens from Water to Methanol
A F Danil de Namor and R Traboulssi, Department of Chemistry, University of Surrey, Guildford, Surrey, GU2 5XH (UK)

The formation of antibody–antigen (hapten) complexes by combination of antibody molecules with the corresponding hapten is one of the most important processes in inmunology.

The stablility of antibody–hapten complexes is due to the contribution of a number of intermolecular forces (hydrogen bonding, hydrophobic and ionic interactions as well as van der Waal's forces and steric repulsive forces). The interactions being the same as those which contribute to the configurational stability of proteins and other molecules. One of the major hydrogen donor groups present in antibody–hapten interactions is the hydroxyl group.

This paper reports the solubility, thermodynamic solubility products and solution free energies of a number of haptens containing ortho–meta and para benzoate ions in water and in methanol at 298.15K.

The results of conductance measurements to determine the ion pair formation constants of these haptens in the respective solvents are shown and free energy data for the transfer of these haptens from water to methanol are discussed.

Acknowledgements: The scholarship given by the Hariri Foundation to R T is gratefully acknowledged.

10 00 – 10 20 The Solvation of Fluoride Ions in Nonaqueous Solvents

G T Hefter, School of Mathematical and Physical Sciences,
Murdoch University, Murdoch 6150, W. A., Australia

Unlike the other halides, very little quantitative information is available on the solvation of fluoride ions in aqueous solvents. Even the few data currently available, chiefly from solubility studies, often appear to be seriously in error. This paper reviews fluoride solubility data, and the thermodynamic functions which can be derived from them, for a range of pure solvents and compares them with those for the other halide ions. Some experimental results are also reported for alkali metal fluoride salts in a variety of aqueous–organic solvent mixtures. These results are discussed in terms of specific ion–solvent interactions.

10 40 – 11 00 The Solubility of Silver Halides in Water and in Aqueous Solutions of Alkali Halides at Elevated Temperatures

I A Dibrov, S N Lvov, Leningrad Mining Institute, USSR

The solubility of silver halides is of great interest in Analytical Chemistry, photography, potentiometry, chemistry of complexes, etc.

There are some different methods for measuring the solubility of silver halides (radioactive isotopes, potentiometry etc). The majority of experiments were carried out at room temperatures and the minority at temperatures up to 100°C. It can be accounted for the difficulties in the analysis at elevated temperatures and pressures.

In this paper, the results of computer calculations of AgCl, AgBr, AgI solubilities in the aqueous halides solutions of different concentrations at temperatures 25–300°C are reported. The computer program is based on the principle of minimization of Gibbs energy for multi–component systems. The thermodynamic information for the simple complex ions was taken from Helgeson's reference book on thermodynamic properties of minerals and ions.

All the isotherms of solubility have minimums at the concentrations decreasing in the order $Cl^- > Br^- > I^-$. The rise of temperature is followed with an increase in solubility, the minimum moving to upper concentrations.

The isothermic solubility, S, can be described as a simple function of the concentration of C of alkali halides:

$$S = \frac{L}{C}(I + K_I C + K_2 C^2 + \ldots + K_n C^n)$$

where K_I, K_2, ... K_n are the stability equilibrium constants of halide complex ions containing I, 2, ... n halide atoms, L is the solubility product of a silver halide.

The influence of temperature can be explained in terms of the sign of the entropy differences in different processes.

11 10 – 11 30 Solubilities and Gibbs Transfer Energies of Some Cu(II) Salts in Water – DMSO Mixtures

T K Sreekumar and C Kalidas, Department of Chemistry,
Indian Institute of Technology, Madras 600 036, India

Solubility measurements offer a simple method of determining the Gibbs transfer energies of sparingly soluble salts in mixed solvents. By combining these data with the Gibbs transfer energy of one of the ions of salt by a suitable extra thermodynamic method, the ion–solvent interactions of the ions of the salt in any mixed solvent system can be investigated. In the present work, the solubilities and Gibbs energies of transfer (Reference solvent:water) of a few copper (II) salts viz Cu (II) acetate, Cu (II) benzoate and Cu (II) iodate have been determined at 30°C in water – DMSO mixtures over the whole range of compositions. The transfer energies of the Cu (II) ion and of anions have also been obtained on the basis of nLJP method. Although the transfer energy of Cu(II) acetate increases with the addition of DMSO, it decreases in the case of Cu(II) benzoate and iodate under the same conditions.

For the ions, the transfer energy of Cu (II) ion decreases and that of the anions increases with the addition of DMSO. These results suggest a heteroselective solvation of all the salts in water – DMSO mixtures.

11 40 – 12 00 Thermodynamics of Electrolyte Solutions 1

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We have studied the thermodynamics of electrolytes at extreme dilutions. Experimentally, by measuring EMF of a Ag/AgCl/HCl(aq,c)/H_2/Pt cell at 25°C down to c = 5E–5mol/dm^3 in a high precision measuring chamber. Theoretically, by performing some very extended Monte Carlo simulations on the primitive model of electrolytes using up to 1000 ions and several millions of configurations. The Debye–Hückel limiting law (DHLL) was verfied directly experimentally as well as theoretically. The standard oxidation potential for the Ag/AgCl electrode and the *first deviation* from DHLL is found for the first time without using circulatory arguments concerning the functional form of $\ln\gamma_\pm$ vs. $\sqrt{I}$. Below c = 2E–4 mol/dm^3, a deviation is observed caused by the solubility and the diffusion potential of AgCl. The deviation increases rapidly with decreasing concentration.

The Monte Carlo simulations demonstrate, that only the contact distance between the positive and the negative ion is of importance for the thermodynamic properties of single salts in solution. This is just as in the traditional Debye–Hückel theory. However, the Debye–Hückel theory as well as the MSA theory grossly exaggerates the first deviation from DHLL at extreme dilution for any given value of the contact distance. Calculated heat capacities as a function of κa differ qualitatively from the DH– and MSA–curves at a Bjerrum parameter around 1.5. A Monte Carlo method for exact calculation of single ion activity coefficients is presented and used to control the results.

12 00 – 12 20 Thermodynamics of Electrolyte Solutions 11

J B Jensen and T S Sørensen
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Extensive measurements are presented of the mean ionic activity coefficients for KF and KCl in aqueous solutions at 25°C. The concentration range investigated was from 2E–4 to 3–4 mol/dm^3, and the activity coefficients were measured in pure as well as mixed solutions. As electrodes, we used high precision Ag/AgCl, Valinomycin (K^+) and LaF_3(F^-) electrodes. The Debye–Hückel limiting law (DHLL) ws verified directly by polynomial extrapolation. A quite peculiar feature seems to be, that the mean ionic activity coefficients y±(KF) and y±(KCl) up to at least above 1 mol/dm^3 do not seem to depend on the composition of the mixture, but only on the ionic strength. Nevertheless, there is clear difference between the curves of lny±(KF) and lny±(KCl) vs. $\sqrt{I}$. This situation corresponds to Harneds rule with a Harned coefficient approximately equal to zero.

Using an approximate statistical–mechanical model (*Generalized DHX*) this behaviour is reproduced using effective ion–diameters around 2.9Å for K^+ and Cl^- and a somewhat higher diameter for F^- (hydration). The ions have to be quite small and not to differ much in size in order for the system to have a Harned coefficient ≈ 0. The more common situation with nonzero Harned coefficients and almost identical *trace activity coefficients* of the two salts at the same ionic strength can also be reproduced by the GDHX–model. The conclusions are backed up by MSA–calculations (formulae of Ebeling and Scherwinski, 1983) and Monte Carlo calculations (method of Sloth and Sørensen, 1988) of *single ionic activities* in mixed electrolytes with three ions.

12 30 – 12 50 Solubilities, Solubility Products and Solution Chemistry of Lanthanon trifluoride–Water Systems*

M P Menon, and J James,
Department of Chemistry
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Georgia 31404, USA

The data on the solubilties and solubility products of lanthanon trifluorides ($LnF_3.0.5H_20$) are very desirable to improve the solubility data base. The values reported in literature for K_{sp} of a given fluoride differ by a factor of 10^3 in some cases. The data for the thermodynamic functions for the dissolution of these fluorides in water and for the stability constants (β_1 and β_2) for the mono– and difluoride complexes of lanthanons are either non–existant or inadequate in literature.

We have determined the solubilities and solubility products of fourteen lanthanon trifluorides using radiometric, conductometric and potentiometric techniques. Our pK_{sp} values for $LnF_3.0.5H_20$ obtained from the above three techniques range from 15.2 to 17.9, 13.0 to 17.2 and 12.6 to 17.4, respectively. Standard enthalpy change for the dissolution of the fluorides measured from the plot of $logK_{sp}$ versus 1/T is positive in each case and falls within the range of 30–60 kJ mol^{-1}. Standard free energy change obtained from K_{sp} values is also positive and falls within the range of 78–103 kJ mol^{-1}. Standard entropy change, on the other hand, is negative and ranges form –47 to –294 J $mol^{-1}K^{-1}$. Although our values for β_1 falls within the range of reported values, those for β_2 are much higher than the published data.

* Research supported by the U S Department of Energy (Grant No DE–FG09–84SR14014)

Wednesday afternoon 24 August 1988

SESSION 4

Solubility of Gases

Co–Chairmen: M Salomon (USA), R Cohen–Adad (France)

14 00 – 14 45 PLENARY LECTURE: Phase Behaviour of Fluid Mixture at High Pressures

W B Streett, Cornell University, Ithaca, New York, USA

15 00 – 15 20 Solubility of Gases in Liquids; Solubility of 10 Gases in Some Alkanols (CH_3OH to $C_{11}H_{23}OH$) at 298.15K

S Bo, R Battino, Chemistry Department
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As part of our continuing effort to obtain accurate gas solubility data in liquid systems of biophysical interest, we report here on the solubilites of He, Ne, Ar, Kr, Xe, N_2, O_2, CH_4, CF_4 and SF_6 in several homologous 1–alkanols n–$C_lH_{2l+1}OH(1 \leq l \leq 11)$. The experiments were conducted at 298.15K and atmospheric pressure, using an apparatus of the BEN–NAIM/BAER design. The OSTWALD coefficents $L(T,P) \equiv c^L_{gas}/c^V_{gas}$ were measured with a precision of about 0.6% (c^L_{gas}, c^V_{gas}... amount–of–substance concentration of solute in the coexisting liquid phase and vapor phase, respectively). Data reduction is presented in some detail (1,2), including estimation of auxiliary quantities. The effect of chain length l upon solubility is shown, and some correlations between L (or the derived HENRY fugacity $H_{2,1}$) and appropriate molecular and/or bulk properties of the gases and solvents are discussed.

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15 30 – 15 50 Solubility of H_2S, CO_2 and CH_4 in n–Formyl Morpholine

F.–Y Jou, F. D. Otto and A. E. Mather, University of Alberta, Edmonton, Alberta, Canada T6G 2G6

N–formyl morpholine is a physical solvent which has been proposed for the separation of the acid gases, H_2S and CO_2, from natural and synthesis gas streams. A knowledge of the solubility of these gases is necessary to decide if this solvent has any advantages over those solvents now in use. As well, the solubility of methane is important, since its magnitude is a measure of the loss of hydrocarbons in the solvent. To answer these questions, the solubility of these gases in n–formyl morpholine was measured at five temperatures between 25°C and 130°C at pressures up to about 7 MPa.

The experimental data were correlated by the Peng–Robinson equation of state. Parameters for the n–formyl morpholine were estimated from liquid molar volumes and vapor pressures. Values of the binary interaction parameter were obtained from the experimental data. Using the expressions connecting the values of the binary interaction parameter with the parameters of the Krichevsky–Kasarnovsky equation, Henry's coefficients for the three solutes were obtained.

16 10 – 16 30 Relations Betweeen Solubility of Gases and the Molecular Structure of Hydrocarbonate Solvents

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This paper deals with the equipment, experimental technique and the results of determinations of the solubilities of gaseous propene, 1–butene, isobutene, cis and trans 2–butene in hydrocarbonate solvents as n–alkanes (nC_7 – nC_{10}), isooctane and 1–octene.

Measurements were carried out in an apparatus based on the saturation principle. Partial pressure of the dissolved gas was maintained at 101.35 kPa and measurements were performed in the temperatures range between 288.15K and 338.15K.

Ostwald coefficient, L, Bunsen absorption coefficient, α were evaluated. Enthalpies of dissolution of gases in the liquids and entropies of solutions were calculated from the linear dependence of the logarithms of the mole fractions, x_2 versus the inverse absolute temperatures.

The variation of the solubilites is discussed as a function of the nature of the solute and the molecular structure of the solvents.

The Lennard–Jones parameters and the Bunsen coefficient, α were correlated in a predicted equation for the determination of solubility of gases.

16 40 – 17 00 Solubility of Light Hydrocarbons in Mixtures of n–Alkanes

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We have determined experimentally the solubility of propane and n–butane at 25°C in the following binary mixtures of normal alkanes: $C_8 + C_{14}$, $C_8 + C_{15}$, $C_9 + C_{13}$, $C_{10} + C_{13}$ and $C_{12} + C_{15}$. Results were also obtained at 50°C for the same solutes in $C_8 + C_{14}$ and $C_{12} + C_{15}$. Several different compositions of the solvent mixtures were studied in each case. Values of the Henry's law constant were derived from the solubility data for propane and n–butane in both the pure n–alkanes and as a function of composition for the solvent mixtures.

The corresponding State principle for chain–molecule liquids was used to calculate Henry's law constants for the systems experimentally studied in this work. The calculated values of Henry's constant for the two solutes in pure solvents at 25 and 50°C agree reasonably well with the experimental values for the 22 systems studied. The agreement between calculated and experimental Henry's constant for a given solute in a mixture of solvents is very good through the use of the well known Bronsted Principle of Congruence.

17 10 – 17 30 "Salting Out" by a Gas – Phase Separation Caused by a Gas Dissolving into a Liquid Mixture

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A phase separation occurs when butane gas dissolves into certain mixtures of t–butyl alcohol (2–methyl–propan–2–ol) and water, at low temperature.

In conventional "salting out" of non–electrolytes from water, the affinity between the added salt and water is exploited. In the case of butane with t–butyl alcohol and water, the affinity between the hydrocarbon and the alcohol is being exploited to achieve a phase separation.

The conditions for the separation, and the composition of the phases separated, have been related to the solubility of butane in the aqueous alcohol mixtures involved.

Thursday morning, 25 August 1988

SESSION 5

Macrocyclic Systems and Organic Electrolytes

Co–Chairmen: L H Gevantman (USA); C Guminski (Poland)

08 30 – 09 15 PLENARY LECTURE: Macrocyclic Ligands, Influence on Electrolyte Solvation and Solubility

B.G.Cox, Stirling University, UK
H.Schneider, Max Planck Institute, West Germany

Joint Lecture

09 30 – 09 50 Solution and Ionization of Aminosulphonic Acids in Dimethylsulfoxide

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Aminosulfonic acids are bifunctional compounds of interest particularly because of their structural relation to amino acids. We have determined some of the thermodynamic parameters for the solution and ionization, in Me_2SO and water, of 4 aminosulfonic acids HA: $NH_2-(CH_2)_n-SO_3H$ (n = 0,1,2) and $NH_2-C_6H_4-SO_3H$. Potentiometric and calorimetric methods were used.

The solubility of the 4 acids in Me_2SO are either nearly equal or lower than in water but the enthalpies of solution are 15–40 kJ mol^{-1} more exothermic in Me_2SO. The 3 aliphatic acids are much weaker ($2.0 \leq \Delta pK_a \leq 5.3$) in Me_2SO than in water and their heats of ionization are some 30 kJ mol^{-1} more endothermic in Me_2SO. The discussion of our results is based on comparisons with corresponding data for related substituted amines and ammonium ions, and sulfonic acids and sulfonate ions. We conclude that the aminosulfonic acids are essentially present as dipolar ions $NH_3^+-R-SO_3^-$ in Me_2SO just as in water. The poor solvation in Me_2SO of the $-SO_3^-$ group, particularly when it is attached to the aliphatic carbon chain, is noteworthy.

10 00 – 10 20

SOLID-LIQUID EQUILIBRIA IN PHENOL-PHENOL AND PHENOL-COMPLEXING AGENT SYSTEMS

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Solid-liquid equilibrium (SLE) phase diagrams in phenol-isomeric cresol, cresol-cresol, phenol-dihydric phenol, urea-phenol, urea-cresol, urea-xylenol and a few ternary urea-cresol-cresol and urea-phenol-aromatic hydrocarbon systems have been studied both experimentally and theoretically. Phase boundaries have been described by the use of well-known liquid phase activity coefficient correlations. Molecular conditions have been discussed for the formation of phenol-phenol and phenol-urea complexes with particular reference to hydrogen bond formation, crystal lattice type and molecular geometry of the complex.
New thermochemical and thermodynamic data measured by differential scanning calorimetry and by IR spectroscopy techniques for pure components and for complexes are reported. The data were used for the evaluation of selected correlation equations.
Crystallization fields and invariant points in ternary systems are considered and discussed at more length in the urea-phenol-naphthalene system.

10 40 – 11 00 Solubilization of Tetramethylammonium Salts by Their Homologues in Chloroform

J. Czapkiewicz, Faculty of Chemistry,
Jagiellonian University, Kraków, Poland

The low solubility of typical inorganic tetramethylammonium salts in chloroform has been well demonstrated and it is generally assumed that in the concentration range attainable for experiment, these salts exist predominantly in the form of ion pairs. The results of our recent vapour pressure osmometry studies carried out on homologous alkyltrimethyl–ammonium bromides in chloroform indicate that ion pairs aggregate in this solvent and that the tendency to n–merization increases with the decrease in length of the alkyl chain.[1] Because of solubility restrictions such studies could be extended down to ethyltrimethylammonium bromide only. It is shown, however, that the solubility of this salt and of several title compounds in chloroform increases significantly in the presence of homologous alkyltrimethylammonium salts of common or different counter–ions.

It is suggested that this effect is due to incorporation of the scarcely soluble salts into the structure of reversed micelles formed by the co–solutes. Solubilization of simple electrolytes through the formation of mixed organized assemblies in chloroform seems to be a potential tool in extraction and separation procedures.

1 Part of the results submitted for publication in J. Colloid. Int. Sci.

11 10 – 11 30 Thermodynamic Studies of Thallium (I) Halide Formation In 1,3 – Dimethyl – 2 Imidazolidinone

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1,3 – dimethyl – 2 imidazolidinone (DMI) is a donor solvent of an amide (urea) derivative with a five–membered ring structure. Although the donor number of DMI is unkown at present, it is a good solvent for various organic and inorganic compounds and has a high polarity with the dipole moment of 1.36×10^{-29}Cm. However, stability of halogeno metal complex in DMI has not been discussed.

The thermodynamic quantities of thallium (I) halide (TlX) in DMI were determined from the solubility products (K_{so}) of TlX by potentiometric titration. The K_{so} of TlX in DMI decreased in the order of TlI > TlBr > TlCl for halide ion (X^-), which is the reversed order in water. The Gibbs energies of TlX in DMI at 25°C is calculated buy use of $\log K_{so}$ were compared with those in N,N–dimethylformamide (DMF) and propylene carbonate (PC). The order of the stability of TlX in these three solvents is PC > DMI > DMF.

The donor number of DMI was estimated to be 20–23 by measuring the half–wave potentials for polarographic reduction of several uni– and bivalent metal ions referred to tetraphenyl–arsonium tetraphenylborate. By comparing the donor number of DMI with those of DMF and PC, the order of PC > DMI > DMF for stability of TlX in three solvents is reasonably interpreted.

11 40 – 12 00 **Enthalpies of Complexation and Transfer of Lanthanides (III) Cryptates**

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Data on the transfer of single–ions among different solvents are extremely useful parameters in the study of interactions between ions and solvents. Up to now,there has been only limited information on single ion transfer data for multi valent ions from water or any other reference solvent to non–aqueous media. This paper reports enthalpy data for the transfer of lanthanide (M^{3+} = La^{3+}, Pr^{3+},Nd^{3+}) cations among dipolar aprotic solvents obtained from:

a Heats of solution of lanthanide salts in the appropriate solvents

b A thermodynamic cycle using heats of complexation data of lanthanide (III) cations and cryptand 222 (222) in dipolar aprotic media as described by the process: $M^{3+}(s) + 222(s) \rightarrow M^{3+}222(s)$.

Acknowledgement

The authors are grateful to the Commission of the European Communities, Directorate General for Science,Research and Development (DG12,Stimulation Action) for the financial support given to this project. The assistance given by the British Council to MCR is gratefully acknowledged.

12 10 – 12 30 **Use of [Fephen$_2$(CN)$_2$] to Probe H–Bonding, Hydrophobic Interaction and the Role of Urea**

M.P. Byfield, V.L.Frost, J L J.Pemberton, J.M.Pratt and V.J Ramdas, Department of Chemistry
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The intense charge transfer bands of the complex [Fe^{II}(o–phenanthroline)$_2$(CN)$_2$] (1) are very solvent–dependent, moving from 516 nm in H_2O to 625 nm in acetone and showing a correlation with Reichardt's E_T parameter [1] and Mayer's acceptor number AN [2]. Our interest in the role of weak interactions (in reactions of metallo–enzymes, froth flotation of minerals, etc) prompted us to explore the possible use of I to probe H–bonding and hydrophobic interactions and the role of urea.

(1) We obtained crystals suitable for X–ray analysis which enabled us to establish I as the cis–isomer.

(2) We have reported [3] that the spectrophotometric titration of a dicyano–Co(III) corrinoid (derivative of B_{12}) in CCl_4 with MeOH occurs in two stages which correspond (isosbestic points, stoichiometry of binding) to the successive formation of two specific H–bonds. We now find that the titration of I in $CHCl_3$ with MeOH also involves two stages (ie successive formation of the two H–bonds) but the isosbestic points are distinctly "broken", indicating some additional effects; the spectra should therefore provide a sensitive indicator both of the number of H–bonds and of further changes in the solvation sheath.

(3) The low solubility of I in water is markedly enhanced by urea, without any significant change in the absorption spectrum. The optical density of the saturated solution increases with the square of the urea concentration, indicating interaction with two molecules of urea. (Preliminary studies show that the solubilities of benzene and phenol also increase more than linearly with the urea concentration).

This unexpected stoichiometry indicates that urea exerts its solubilising effect through specific interactions and not, as usually assumed, through a non–specific "structure–breaking" effect. Noting (a) the tendency of H_2O molecules to cluster into

chains and rings [4] and (b) the recent evidence that H_2O (like Et_2O) acts as a "donor" towards benzene [5], we suggest that H_2O can form structures such a cyclic H–bonded hexamer with chair conformation, in which the six "free" protons all occupy equatorial positions and the six "free" lone pair axial positions. Interaction with a benzene ring (acting as acceptor to 3 lone pairs) and urea (forming H–bonds with two of the three lone pairs on the other side) could provide the basis for cooperative interaction in the urea–water–aromatic system. The alternative boat conformation could also facilitate interaction both with benzene (as acceptor for 4 lone pairs) and urea (H–bonds with 2 lone pairs).

References

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2 Toma and Takasugi, J Soln Chem, 1983, 12, 547

3 Markwell, Pratt, Shaikjee and Toerien, J Chem Soc Dalton 1987, 1349

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5 Wormald and Lancaster, J Chem Thermodynamics, 1985, 17, 903

Thursday afternoon, 25 August 1988

SESSION 6

Polymers, Miscelles and Miscellaneous Topics

Co–Chairmen: J M Pratt (UK); C Kalidas (India)

14 00 – 14 45 PLENARY LECTURE: Title to be announced
R van der Haegen, DMS Research, Netherlands

15 00 – 15 20 Recent Advances on Statistical Thermodynamics of Polymer Solutions
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Based on our thermodynamic theory and topological structure theory as well, the statistical thermodynamics of multicomponent macromolecular solutions consisting of polymer, solvent and nonsolvent (precipitant) is developed. In this context, the chemical potential of the main component (polymer) is perturbation–theoretically investigated in dependence on the concentration column vector (regarding the volume fraction of each thermodynamic component as a vector component) in relation to the unperturbed reference state and the relative "strength of perturbation" which corresponds to the volume fraction of the nonsolvent.

The theory is applied to the phase separation in quasiternary polymer solutions, occurring after the addition of precipitant. In the case of a continuous polymer distribution the theory presents itself as a continuous macroscopic statistical–thermodynamic approach to the phase separation in quasiternary macromolecular liquid systems in dependence on polymer concentration, molecular weight, temperature and pressure. The theory is scrutinized experimentally for falsification at different polymer + solvent + nonsolvent systems, such as for example: (i) polystyrene + benzene + methanol; (ii) poly (methyl methacrylate) + benzene + cyclohexane; (iii) nylon 6 + m–cresol + cyclohexane (or petroleum ether). Our theoretical approach is corroborated furthermore by numerous experimental results taken from the literature, as well as with the aid of a quantitative reliability theory of polymer fractionation.

15 30 – 15 50

Excess Thermodynamic Properties of Some 2–Alkoxyethanol + Water Systems

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The 2–butoxyethanol + water system possesses a closed miscibility gap, with a maximum temperature range 50–130°C (at x_B = 0.08) and a maximum composition range x_B = 0.025–0.19 (at 90°C). The composition dependence of its thermodynamic properties at 25°C have led to the classification of 2–BE as a borderline surfactant.

We have determined values for a variety of thermodynamic differential coefficients for the systems $H(CH_2)_n OC_2H_4OH + H_2O$ (n = 0, 1,2,4) from densities and ultrasonic velocities measured in Clermont–Ferrand, together with isobaric heat capacities and expansivities extracted from the literature.

Plots of the differential coefficients for these systems reveal some dramatic changes in composition dependence which become more prominent with successive extension of the hydrophobic alkyl group. An attempt to quantify these characteristics will be given in a companion paper.

Some suggestions are offered concerning thermodynamic characterisics of micro–dispersed and macroscopic phase separations.

16 10 – 16 30

Four–Segment Model Analyses of Some Excess Thermodynamic Properties of Alkoxyethanol and Water Systems

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The segmented composition model for the thermodynamic properties of binary aqueous systems has undergone a number of evolutionary stages, primarily in the realm of parameterization. The effectiveness of the approach has proved to be particularly significant when dealing with systems which show a tendency to mimic micellar and bilayer behaviour.

A modified version has been developed which embodies some of the characteristics of pseudophase and mass action models. This model, which will be described in some detail, has been applied to alkoxyethanol + water systems. The results will be discussed in terms of the relative tendencies towards the formation of structured organic aggregates.

16 40 – 17 00 Use of the Friedman–Type Excess Functions For The Study of Interactions in Functional Group Carrying Ionic Polymers

A Marton, J Inczédy
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Using the concentrated electrolyte solution model of the ion exchange resins equations were derived for the composition dependence of the selectivity coefficient. From the experimentally obtained functions ln K' vs. $\bar{x}$ the derived equations make possible the calculation of the thermodynamic exchange constant as well as the so called free energy interaction parameters introduced by Friedman. The variation of the latter quantities is a function of the crosslinking of the polymer matrix and the size of the exchanging counter ions.

A knowledge of these parameters can be useful in the understanding of the thermodynamic state of the internal electrolytes in industrially or biologically important polymers carrying immobilized functional groups.

Thursday afternoon 25 August 1988

SESSION 7

Studies of Pharmaceuticals and organic–non–electrolytes

Co–Chairman: H L Clever (USA), F. Arnaud Neu (France)

17 10 – 17 55 PLENARY LECTURE: Solution Processes of Pharmaceutical Importance,

A Beezer, Royal Holloway and Bedford New College
London University, (UK)

Friday morning 26 August 1988

09 30 – 0950

An Analysis of Cyclohexane–Water Partition Coefficients and a Comparison of Various Solvent–Water Partitions

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The distribution of a wide variety of nonelectrolytes between water and cyclohexane can very well be correlated through the equation:

$$\log P = c + s.\pi_2^* + a.\alpha_2 + b.\beta_2 + m.V_2$$

where P is the cyclohexane–water partition coefficient and π_2^*, a_2, β_2 and V_2 are solute properties, viz: dipolarity, hydrogen–bond acidity, hydrogen–bond basicity and volume (taken as Leahy's intrinsic volume, V_I). For 78 solutes, including alcohols, phenols, and aromatic and aliphatic hydrocarbons, ethers, esters, ketones, amines, acids, etc, the overall correlation coefficient is 0.9975 and the standard deviation in logP only 0.114 units. The main factors governing distribution are the solute α_2, β_2 (and to a lesser extent) π_2^* parameters that favour water and the solute V_I parameter that favours cyclohexane. A comparison of factors influencing a variety of solvent–water partition coefficients will be presented.

10 00 – 10 20 Structure Characteristics for Liquid 1, 1 Dimethylhydrazine - Water Solutions from Equilibrium Vapour Pressure Measurements

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Structure characteristics for associated liquid mixtures, based upon cluster statistics and mass balance, have been determined for 1,1 dimethylhydrazine (UDMH) and water solutions from equilibrium vapour pressure measurements versus concentration at 65.83°C and 74.07°C. The Gibbs free energy of mixing from thermodynamic calculations has been partitioned into enthalpy and entropy terms attributed to cluster formation at infinite dilution and ideal mixing of the cluster.

The behaviour of the partitioned enthalpy and entropy terms versus solution concentration is provided for the UDMH–H_2O system.

10 40 – 11 00

Graph Theoretical Indices as Structure Descriptors in Studies of Structure–Solubility Relationships of Pharmaceuticals

A. Regosz, T. Pelplińska, K. Ośmialowski and R. Kaliszan
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Solubilities of 16 derivatives of 5–nitrofuran in water, of 12 tetracycline antibiotics in 22 organic solvents and 10 sulphonamides in water at various pH were analysed. The structure of agents considered (both solutes and solvents) was characterized numerically by means of empirical and semiempirical structural descriptors like dielectric constant, the solvent polarity parameter of Reichardt et. al, n–octanol–water partition coefficient, the hydrophobicity constant of Hansch and Leo, dissociation constant, molecular refractivity, van de Waals volume and molecular surface area. The structural indices derived from the graph theory were calculated and analysed.

In the case of 5–nitrofurane derivatives the structural information content index of Basak et. al, of zeroth order, SIC_0, provided most of the information about solubility of the solutes in water as compared to the other structural descriptors studied. The index SIC_0 combined with the hydrophobicity constant, Σ_f, allowed prediction of solubility at the 0.0003 significance level.

For the description of solubilities of individual tetracyclines in various solvents in the information content indices of zeroth and first order, of Sarkar et. al, IC_0 and IC_1 and the structural information content index of first order, SIC_1, appeared equally good descriptors of solvents as the empirically derived polarity parameter $E_T(30)$, and significantly better than dielectric constant.

The topological shape index of Kier, of first order, K^1, appeared the most significant solubility descriptor of all the parameters studied in the case of sulphonamides. Solubility prediction at the 0.003 significance level was obtained combining the K^1 parameter with the melting point. Also, the indices SIC_0, CIC_0, TIC_0, were found significant in structure–solubility relationships studies of sulphonamides.

11 10 – 11 30 Solubility of Some Six–Carbon Hydrocarbons in Liquid Nitrogen

E Szczepaniec–Cieciak, L.Ulman* and M.Kurdziel
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The solubility of hexane, 1–hexane, 1–hexene and cyclohexane have been measured in liquid nitrogen at a temperature of 77.4 K by the filtration method.

The experimental approach and the results will be discussed. The results have been compared with the solubilities calculated on the basis of the Scatchard–Hildebrand equation. Correlations between the solubility of C6 hydrocarbons in liquid nitrogen and some properties of solutes are presented.

Acknowledgement: This work has been financially supported by the Institute for Low Temperature and Structure Research, Polish Academy of Sciences.

* Regional Laboratory of Physicochemical Analysis and Structure Research, Jagiellonian University.

11 40 – 12 00 Molecular Motions at Fast Mixing Processes in Open Liquids

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Molecular motions at fast mixing processes in open liquids are linked to the thermodynamic forces and state variables as also to their irreversible changes, being based on concentration differences and fluctuations. The molecular interactions rest mainly on two effects: (i) the diffusion, and (ii) the molecular mobility. Their influences in incompressible, binary ideal liquids are investigated. By means of the Langevin equation the total force is decomposed into the external contribution, the regular friction force, and a rapidly fluctuating irreversible statistical part. In this way, the mean behaviour of an ensemble of particles just as that of a single particle is treated. Some important limit cases are analysed, as eg with regard to the brems–time. At the onset of the dispersion of a particle cloud, for example, the mean–square displacment is proportional to the time square, whereas after long times of observation a pure diffusion behaviour is to be expected. Numerical values for molecular motions in liquid mixtures can be estimated. For the brems–time eg one finds some 10^{-14}s, and for the brems–way about 1/100 of a molecular diameter. Finally, there results an estimate of the course–time of concentration fluctuations which shows to be proportional to the cube–root of the mean volume of a local concentration fluctuation.

INVITED LECTURE AND POSTER SESSION

Tuesday Evening 23 August 1988

Chairman: P.G.T Fogg (UK)

19 30 – 20 10 Dissolution of An NaCl Crystal With the (111) and (–1–1–1) Faces

H Ohtaki* and N. Fukushima, Department of Chemistry,
Tokyo Institute of Technology at Nagatsuta, Nagatsuta–cho,
Midori–ku, Yokohama, 227 Japan

The dissolution process of an NaCl crystal with the (111) and (–1–1–1) faces, the former consisting of only sodium ions and the latter only chloride ions, as well as the {100} faces, in water has been demonstrated by means of molecular dynamics simulations. Ion–ion, ion–water and water–water intermolecular interactions are assumed to be described in terms of the Tosi–Fumi, Popkie–Kistenmacher–Clementi, and Matsuoka–Clementi–Yoshimine potentials, respectively. Twenty–eight sodium ions, twenty–eight chloride ions and 189 water molecules were placed in a box having the side–length of 2000 pm. Collision of water molecules with the walls of the box was assumed to be completely elastic. The temperature of the system was kept at 25°C during the simulation procedure, which was carried out for 7 ps (the time step Δt = 1.0 x 10^{-15}s, the total steps performed were 7000) after starting dissolution of the NaCl crystal. The first three ions dissolved were chloride ions at the corners of the crystal. The fourth one liberated was a chloride ion on the (–1–1–1) face. As we have seen in the previous simulation using another NaCl crystal with the {100} faces [1], no sodium ion was removed from the crystal surface within 7 ps even sodium ions on the (111) face were exposed to the bulk water phase. Repulsive forces arising between the chloride ions and water molecules which tend to hydrate sodium ions around the chloride ions are the force for separating the chloride ions from the crystal.

1 H.Ohtaki, N. Fukushima, E. Hayakawa and I. Okada, Pure and Appl Chem, in press

Poster Session

P1 Solubility of $Ce(SO_4)_2.nH_20$

E M Kirmse
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Kothen, East Germany

This paper reports the solubilities of $Ce(S0_4)_2.nH_20$ (n = 2,4,6) in H_2S0_4 solution (H_2SO_4 = 1.5; 3.0; 4.5 mol dm^{-3}), at 298, 308, and 318K, respectively. The results are given in terms of the anhydrous salt.

P2 Solubilities of Lanthanides Sulphates in Sulphuric Acid

T M Kirmse
Pädagogische Hochschule "Wolfgang Ratke"
Kothen, East Germany

This paper reports the solubilities of lanthanide sulphates ($Ln_2(SO_4)_3 8H_20$) in sulphuric acid (3mol dm^{-3}) in the 298–328K temperature range.

P3 Enthalpies of Solution of Pyridine Derivatives in Weakly Polar Organic Solvents

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Heats of solution of pyridine, α–picoline, α–, α'–bipyridyl, and diphenyl in weakly polar organic solvents were measured at infinite dilution at 298.2K by means of calorimetry ("constant temperature environment" calorimeter). Heats of transition (ΔH_{trans}) from cyclohexane and heats of solvation (ΔH_{solv}) of these compounds were calculated. On the basis of ΔH_{trans} and ΔH_{solv} the influence of interactions of the "additional" nitrogen atom lone–pair and π–electrons of the "additional" aromatic ring of bipyridyl with solvent molecules was evaluated. Heats of transition and solvation of these compounds were compared with the previously obtained results for other pyridine derivative (4–cyanopyridine, 2–chloropyridine, 3–chloropyridine, 2–aminopyridine, 2,4–lutidine, 2,6–lutidine). These are discussed in terms of steric effects and donor–acceptor interactions of the n–σ, n–π, π–π and π–σ type between the solutes and environment.

P4 A Closed Region of Three–Phase Equilibrium in Ternary Water–Organic Systems

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In some ternary systems the volume of three–phase state in the co–ordinates $T–x_1–x_2$ (T–temperature of dissolution, x_i–mole fraction of i–component) is enclosed between two limiting tie–lines. The water–decane–2–butoxyethanol and W–D–3–picolin systems belong to a small number of systems of the given type.

The temperatures of phase transformations in heterogeneous mixtures in these systems were determined by polythermal method in the temperature range of 280–350K. In accordance with completely pure substance, liquid phases were arranged according to the height of ampoules and were conventionally designated as: upper (L_1) – decane, middle (L_2) – organic, lower (L_3) – aqueous.

It is stated that with the increase of temperature in both systems the formation of three liquid phase of this state are performed according to the second scheme of Schreinemakers. In the first case, L_2 and L_3 take part in critical phenomena in the presence of L_1. In the second case, at the transition of 3L = 2L critical phenomena are accomplished between phases L_1 and L_2 in the presence of aqueous phase. The limiting tie–line $K_{12}L_3$ on the state diagram is directed to the decane–2–butoxyethanol(3–picolin) system.

P5 Development of Group–Contribution Mixing Rules for Equations of State and their Use in the Calculation of Supercritical Fluid Solubilities

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The use of supercritical fluid extraction has become much more common in recent years. One of the problems with designing such processes is often the lack of a reliable means of predicting the solubility of given solute in a given solute.

This paper discusses the extension of a group–contribution activity coefficient model so that it may be used in the mixing rules for an equation of state. Some of the problems and advantages of adopting such an approach will be discussed. Also, some calculations for a specific group–contribution model and a specific equation of state will be given and compared with experimental results.

P6 An Evaluation of the Solubility of Hydrogen Chloride Gas in Aliphatic Alcohols as a Function of Temperature and Pressure

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The solubility of hydrogen chloride is reported in a number of normal and branched chain alkanols as a function of temperature and hydrogen chloride partial pressure. In general the hydrogen chloride solubility at one atm partial pressure is large, between 0.5 and 0.6 mole fration at 273K, and decreases as the temperature increases with approximately one–sixth power of the partial pressure. Thus, errors in measurement of the partial pressure result in only one–sixth the error in the solubility. Graphical and tabular values of the tentative solubility values are presented and discussed.

P7 **Determination of Gas–Liquid Partition Coefficients and their use in the Evaluation of Phases for Chemical Sensors**

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The change in characteristic frequency when a surface acoustic wave (SAW) device coated with a film of stationary phase is allowed to absorb a vapour from the gas is given by:

$$\Delta fv = \Delta fs.Cv.K/\rho$$

where Δfv is the frequency shift on exposure to a vapour stream of concentration Cv, Δfs is the frequency shift due to the coating itself, K is the solute gas–liquid partition coefficient, and ρ is the coating density. We have determined values of Δfv for (a) a series of solutes with a given coating and (b) a series of coatings with a given solute. In parallel with these experiments, we have obtained values of K for the same two series, using the technique of gas–liquid chromatography, where the SAW coating is used as the GLC stationary phase. It is shown that the patterns of responses predicted through the GLC experiments as $\Delta fv = \Delta fx.Cv.K^{GLC}/\rho$ are the same as those found experimentally using coated SAW devices. Hence the GLC can be used to evaluate possible coating materials and, by the technique of multiple linear regression analysis, to predict SAW responses for a multitude of vapours.

P8 Thermodynamic Studies of Alkali Metal Dibenzocryptates in Dipolar Aprotic Solvents

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Enthapies and entropies of complexation of metal (1) cations and dibenzocryptand 222 in a number of dipolar aprotic solvents at 298.15K are reported. The decrease in complex stability for metal–ion dibenzocryptates with respect to metal–ion cryptates is observed. In most cases, this is controlled by the higher entropy loss which occurs during the process of complexation of metal (1) cations with dibenzocryptand 222 with respect to the same process with cryptand 222. A linear correlation[1] between entropies of solvation of metal (1) cations and entropies of complexation of these cations in the dipolar aprotic solvents is found.

1 A.F. Danil de Namor, J.Chem Soc, Faraday TransI, 1988, 84 2441

Acknowledgments: The scholarship given by the Overseas Development Administration (UK) and the British Council to FFS as part of the Surrey/San Agustín (Peru) project in Chemistry is gratefully acknowledged.

P9 Measurement and Calculation of Transfer Enthalpies of Potassium Chloride from Water to Water – Dioxane Mixture

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Molar integral enthalpies of solution at low concentration of KCI have been measured at 298.15K in water–dioxane mixtures (40.01, 48.38, 55.43 and 62.72 mass per cent dioxane) using an isothermal dilution calorimeter. Molar enthalpies of solution at infinite dilution were calculated by applying a simple linear equation. These data and the corresponding literature value of KCI in water were used to obtain the enthalpies of transfer of the investigated salt from water to water–dioxane mixtures. The dependence of transfer enthalpies on the solvent composition is discussed qualitatively.

To investigate the possibility of theoretical description on this thermodynamic transfer property, the theory of scaled particle modified by Born electrostatic effect was used. The agreement between the theoretical expectation and experimental result was satisfactory.

P10 Investigation of Physico–Chemical Properties of Chromium Species i Water Systems

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The preciptation of chromium hydroxyde at 20°C was investigated experimentally in large range of chromium nitrate concentration and pH–values.

The apparent solubility constants and some hydrolytic constants were calculated b means of graphical analyses of experimental solubility curve (pH vs.total chromiu concentration) and suitable segments on pH–axis: *KsO, *Ks1, *Ks2, *Ks3, *Ks4, *K *K2, and $^{*}\beta 3$.

The adsorption of different ionic species of chromium was also investigated. Adsorptic of chromium (111), which was present as Cr^{3+} and $Cr(OH)_2^+$ was studied on colloid particles of SiO_2 (Ludox SM 30) as a model substance, and $CR(OH)_4^-$ on particles $Mg_3Si_2O_5(OH)_8$ (Chrysotile), as a natural substance in water systems. Adsorption Cr (V1) which was present as CrO_4^{2-} and $HCrO_4^-$ was also investigated on colloid particles of $\gamma - Al_2O_3$ (Alon) as a model substance in water. Experimental data a presented in the forms of Langmuir adsorption isotherms. From adsorption curves t adsorption constants K and adsorption capacities Γ_∞ of different chromium species we calculated as well as the specific surface occupied by one molecule of adsorbate.

P11 A Polymer–Polymer Miscibility Database

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A database giving information on polymer–polymer miscibility has been designed using the SPIRES database system on the IBM 3081 mainframe computer on our campus. This database should be up–to–date in the fall of 1989. This poster will illustrate the type of information in the database and the items that can be searched. Some possible report formats will be illustrated. Continuous updating of this database is planned after 1989. Plans are also being made to allow others to use this database for a small fee after 1989.

P12 Excess Enthalpies of Solution of Some Nitriles in Dodecylsurfactants Micellar Solutions

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This paper is a part of a series dealing with thermodynamic investigations of water–surfactant–additive ternary systems undertaken in our laboratory. Our attention is focused on the distribution constant of the additive between the aqueous and the micellar phases and on its thermodynamic properties in both phases. These quantities can be evaluated at the same time from the experimental thermodynamic properties by using an approach based on the pseudo–phase transition model for micellization and on a mass action model for the additive. From enthalpimetric studies the standard free energies, enthalpies and entropies of transfer of primary and secondary alcohols from water to dodecyltrimethylammonium bromide DTAB,[1,2] sodium dodecylsulfate NaDS[3] and dodecyldimethylamine oxide DDAO[4] micellar phases have been determined. From the analysis of these quantities it was shown that DDAO and DTAB micelles show towards alcohols comparable affinity which in turn is smaller than that of NaDS micelles. In order to understand if this interesting result can be generalized, we have determined the excess enthalpies of solution of nitriles with respect to water in micellar solutions of DTAB, DDAO and NaDS at 25°C. They were measured by mixing aqueous solutions of nitriles with micellar solutions by taking as baseline of the mixing process the dilution of surfactant solutions with water. Because of many problems the quantities related to NaDS were not razionalized. As far as DTAB and DDAO are concerned, the standard free energies of transfer of nitriles from the aqueous to the micellar phases put into evidence that the cationic micelles show a greater affinity towards nitriles than the nonionic ones. Also, they indicate that the solubilization of nitriles occurs in the palysade layer of micelles because of the strong hydrophilic and hydrophobic interactions betwen micelles and solutes. Finally, the standard enthalpies of transfer are comparable in both surfactants being always slightly positive.

1 R De Lisi, S Milioto and V Turco Liveri, J Colloid Interface Sci, 1987, 64, 117
2 S Milioto and R De Lisi, J Colloid Interface Sci (in press)
3 R De Lisi, and S Milioto, J Solution Chem, 1988, 17
4 S Milioto, D Romancino and R De Lisi, J Solution Chem, 1987, 16, 943

P13 Excess Functions of Mixing in Polymers and Low Molecular Weight Solvents

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The excess functions of mixing of hydrocarbons of various structure, alcohols, ketones and chlorine containing organic compounds in glassy polyvinyltrimethylsilane and polyphenyleneoxide, as well as in polydimethylsiloxane rubbers and natural rubber have been determined using inverse gas chromatography. Exothermal character of mixing, high entropy effects and sharp dependence of excess enthalpy and entropy of mixing on the solute molar volume in glassy polymers point out analogies on thermodynamics of sorption in glassy polymers and of dissolution in associated liquids.

P14 Solubility and Solvatocomplexes of Copper (11) and Nickel (11) Acetates in Benzene–Carboxylic Acid Mixtures

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The solubility of copper (11) and nickel (11) acetates in benzene mixtures with $C_2 - C_8$ carboxylic acids increases with the acid concentration: $S_{MAc_2} = a + b.\ c_{RCOOH}$. At low acid concentration (Table) the solid phase is the unsolvated salt and the dissolution reaction is given by:

$$2MAc_{2(solid)} + 2RCOOH\ (soln) \rightleftharpoons [M_2Ac_4(RCOOH)_2](soln).$$

Then, the solubility increases proportionally to the square of the acid activity: $S_{MAc_2} = \beta_{22}\ a^2_{RCOOH}$. As the carboxylic acid exists in dimeric form : $2RCOOH \xrightleftharpoons{Kdim} (RCOOH)_2$, the concentration of active monomeric molecules increases with the square root of the total concentration c_{RCOOH}. As a result, a simple solubility dependence is observed if K_{dim} = Const and the solid phase is inexchangeable.

Salt	RCOOH in mixed solvent	a	$b.10^4$/m.f	ρ	c_{RCOOH}/m.f
$Cu(CH_3COO)_2$	CH_3COOH	0.64±0.04	–0.04±0.5	0.994	0-0.19
– " –	C_2H_5COOH	22.9±1.1	3±5	0.999	0-0.08
– " –	n-C_3H_7COOH	30±2	0.2±10	0.997	0-0.08
– " –	n-C_4H_9COOH	30.9±0.8	4±4	0.999	0-0.08
– " –	i-C_4H_9COOH	31.2±0.8	9±3	0.999	0-0.08
– " –	n-$C_5H_{11}COOH$	24±1	6±6	0.998	0-0.12
– " –	n-$C_7H_{15}COOH$	24.7±2	0.1±0.3	0.994	0-0.10
$Ni(CH_3COO)_2$	CH_3COOH	2.6±0.2	2±4	0.995	0-0.34
– " –	C_2H_5COOH	17.2±1.2	8±6	0.994	0-0.12
– " –	n-C_3H_7COOH	18.4±1.1	3±7	0.996	0-0.12
– " –	n-C_4H_9COOH	25.7±1.0	4±5	0.998	0.0.11

P15 Simultaneous Correlation of Excess Gibbs Free Energy and Enthalpy of Mixing by the Uniquac Equation

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Using data for excess Gibbs free energy, g^{ϵ} and enthalpy of mixing h^{ϵ}, temperature dependent parameters of the UNIQUAC equation have been estimated for 24 binary systems. Fifteen of them include data for g^{ϵ} and h^{ϵ} at more than one different isotherms. These parameters are later tested in predicting g^{ϵ} and h^{ϵ} data simultaneously and representing the effect of temperature on such data. The UNIQUAC equation with temperature dependent parameters can predict larger values of maximum heat of mixing than does the UNIQUAC equation with the parameters independent of temperature.

For estimating the parameters a package program called MINUIT has been employed[1]. The MINUIT includes the simplex method and does not require the derivatives of the objective function with respect to its free parameters.

1 F James and M Roos, Comp Phys Comm, 1975, 10, 343

P16 Transfer and Partition Free Energies of 1:1 Electrolytes in the Water–Dichloromethane Solvent System

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Equilibria and derived free energy data for the transfer and partition of electrolytes and ions in water–organic solvent systems have been reported in a number of papers. For a given electrolyte or ion, results derived from experimental data which refer to the process involving two mutually saturated phases may or may not differ depending on the solvent system under consideration, from data involving the transfer of the same electrolyte or ion between the two solvents in their pure state.

Solubility data at 298.15K for a number of 1:1 electrolytes in dichloromethane are reported. The results are used for the calculation of transfer free energies for these electrolytes from water to dichloromethan according to the process:

$$M^+(H_2O) + X^-(H_2O) \rightarrow M^+(DCM) + X^-(DCM) \qquad (1)$$

Partition data for the process:

$$M^+(H_2O \text{ satd DCM}) + X^-(H_2O \text{ satd DCM}) \rightarrow M^+(DCM \text{ satd } H_2O) + X^-(DCM \text{ satd } H_2O) \qquad (2)$$

involving a number of electrolytes are reported and the free energy values for processes (1) and (2) are discussed.

A set of single ion values based on the $Ph_4As\ Ph_4B$ convention are obtained.

P17 Thermodynamic Properties of Antimony Hydroxocomplex at Temperatures up to 723.15K and 1 – 1000 Bar Pressure

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Sb solubility in water at 723.15K, 500 – 1000 bar total pressure hydrogen fugacity 6–90, and the solubility of Sb_2O_3(cub) at 473.15K, 573.15K and variable total pressure (saturated vapour pressure, 500 and 1000 bar) have been determined.

In all cases the solubility increases with increasing temperature and total pressure. The solubility of Sb decreases with increasing hydrogen fugacity.

It has been found, that $Sb(OH)^{o}_{3(aq)}$ is the main antimony species in solutions of all investigated systems.

Based on published solubility data of senarmontite in water at 298.15K and 473.15K and the saturated vapour pressure, the thermodynamic changes of hydrolysis and properties of neutral antimony hydroxocomplex have been determined.

P18 Solubility of Some Normal Alkanes (C_{20} – C_{28}) in Hydrocarbons

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Solubilities of C_{20}, C_{24}, C_{26}, C_{28} n–paraffins (eicosane, tetracosane, hexacosane, octacosane) in heptane and cyclohexane have been measured by a dynamic method at temperatures ranging from melting point to 275K. Four methods are applied to represent the solute activity coefficients (γ_1) from the so–called correlation equations which describe the Gibbs excess free energy of mixing (G^E): that of Wilson. UNIQUAC and two modified NRTL equations.

The root mean square deviations of the solubility temperatures for all measured data vary from 0.11 to 1.0K and depend on the particular equation used. The best correlation was obtained with the two–parameter equations for the excess Gibbs energy UNIQUAC and the modified NRTL2 one. The existence of solid – solid first – order phase transition in n-alkanes has been taken into consideration in the solubility curves calculations by the use of the following relationship:

$$-\ln x_1 = \frac{\Delta H_{m_1}}{R}\left(\frac{1}{T} - \frac{1}{T_{m_1}}\right) - \frac{\Delta Cp_{m_1}}{R}\left(\ln\frac{T}{T_{m_1}} + \frac{T_{m_1}}{T} - 1\right) + \frac{\Delta H_{tr_1}}{R}\left(\frac{1}{T} - \frac{1}{T_{tr_1}}\right) + \ln\gamma_1$$

where ΔH_{tr_1} and T_{tr_1} stand for enthalpy of transition and transition temperature of the solute, respectively.

P19 <u>The Effect of Counternaion in System Cation–Anion–Ligand–Solvent on Complex Formation of Calcium Salts with Macrocyclic Ligands</u>

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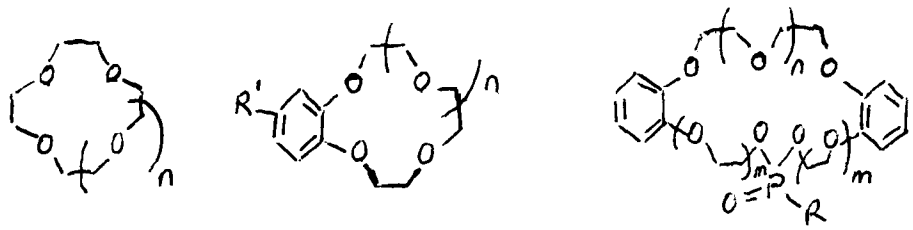
Stoichiometry of complexes, values of the enthalpy, the entropy, and the Gibbs energy changes for the complex formation of calcium salts CaX_2 ($X = Cl^-$, NO_3^-, NCS^-, ClO_4^-) with oxygen – and phosphor containing macrocyclic ligands



n = 1,2,3 n = 1, m = 0, R = Me, Ad
n = 2, m = 0, R = Me, Ad, Ph, OPh
n = 2. ,m = 1, R = Me, Ad

were determined by calorimetric titration and IR spectrophotometric techniques in order to study the influence of ligands geometry, the counteranion effect in the cation–anion–ligand–solvent system on complex formation.

The stoichiometry of 1:1 and 1:2 metal–ligand complexes, the selective binding, the ΔH_i, and ΔS_i (i = 1,2) values are influenced by macrocyclic ring size, functionality of the groups R (R'), and ionic association of the calcium salts. The effect of counteranion on complex formation is explained by the presence in solution of Ca^{2+}, CaX^+ and CaX_2 species.

P20 Thermodynamic Stability of Copper(I) Cation in Nonaqueous Solvents

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Copper(I) cation is unstable in water and in the absence of ligands stabilizing monovalent state it disproportionates to copper(II) and metallic copper. The transfer of the Cu/Cu(I)/Cu(II) system from water (W) to nonaqueous solvent R brings about changes in the relative stabilities of both oxidation states, according to the following cycle:

$$\begin{array}{ccc} 2Cu(I) & \xrightleftharpoons{K_D(W)} & Cu(II) + Cu \\ \Big\downarrow{\scriptstyle 2\Delta G_t[Cu(I)]} & & \Big\downarrow{\scriptstyle \Delta G_t[Cu(II)]} \\ 2Cu(I) & \xrightleftharpoons{K_D(R)} & Cu(II) + Cu \end{array}$$

and the equation:

$$\log K_D(R) = \log K_D(W) + (2.303RT)^{-1}\{2\Delta G_t[Cu(I)] - \Delta G_t[(CuII)]\}$$

The following correlation between $\log K_D$ and transfer free energies of silver(I) and copper(II) has been found:

$$\log K_D(R) = a + b\{2\Delta G_t[Ag(I)] - \Delta G_t[Cu(II)]\}$$

where a = 5.894, b = 0.299 kJ/mol, R = water, dimethylsulphoxide, propylene carbonate, sulpholane, benzonitrile and acetonitrile.
Correlation coefficient = 0.9995.
This correlation can be used for the estimation of the K_D order in other nonaqueous solvents.

P21 Etude de la Competition Electrostatique Entre L'Association et la Solvatation Ioniques

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Le phénomène de solubilité ionique est intimement lié au processus de déplacement des molécules de solvatation par les contre–ions.

Dans le cas des ions alcalins, alcalineux terreux, et des terres–rares, Ln^{3+}, l'association ionique et l'hydratation ionique ont un caractère électrostatique prédominant. Cette situation nous permet d'étudier semi–quantitativement. La variation du profil de concentration: $C_2(r)$ et $C_w(r)$ du contre ion, et du solvant à une distance: r de l'ion central: (Z_1) en fonction des concentrations: C_i^o des ions au sein de la solution.

Modèle Mathématique

Le champ: D(r) (crée par (Z_1) et par l'atmosphère ionique), et le champ: E(r) total sont données par:

$$\text{div } D = 4\pi\Sigma\, Z_i e C_i(r);\ E(r) = (D(r) - P(r))/4\pi = -dV/dr$$

Le calcul de la polarisation: P(r) est basé sur le modèle de (Booth–Grahame):

$$dD/dE = n^2 + (\epsilon_o - n^2)/(1 + bE^2)$$

tenant compte de la saturation diélectrique.

Dans notre modèle, la répulsion entre particules est exprimée en termes de covolumes: b_1 et b_2 des ions et: b_w des molécules d'eau.

D'où: $C_i(r)/C_i^o(r) = A\ Exp(-Z_i eV/kT)$; $C_w(r)/C_w^o\ (r) = A\ Exp(P'.E/C_w.kT)$

$$A = (1 - \Sigma\ C_i b_i - C_w b_w)/(1 - \Sigma\ C_i^o b_i - C_w^o b_w) \text{ et } P' = P(1 - \Sigma C_i b_i)$$

Les calculs montrent que le coefficient d'association: $\alpha = \int_a^q 4\pi\ r^2 C_i(r)dr$, avec ($a = R_1 + R_2$) n'est plus sensible à la distance minimale d'approche: "a" (contrairement au modèle de Bjerrum) (car $C_i(r) \neq \infty$ quand: $r \to a$).

D'autre part, ce modèle permet:

- D'interpréter correctement le phénomène d'hydrolyse des ions Ln^{3+}.
- De prévoir l'existence d'une association de type: 3–1
- De calculer le nombre de molécules d'eau déplacées: $\Delta n = \Delta C_w.\ 4\pi\ r^2 dr$
- Et d'étudier l'influence de la taille des ions sur la solubilité.

P22 Humidity Effects on the Adsorption of Gases and Vapours by Solids

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Gas–solid chromatography has been used to obtain adsorption isotherms by the technique of elution by characteristic point (ECP). A single injection of a gas or vapour suffices to obtain the isotherm, and then the limiting Henry's law constant, K^H, for adsorption at low surface area coverage. About 20–30 solutes are studied per adsorbent, using compounds that have a wide range of properties such as polarity (π_2^*), hydrogen–bond acidity (α_2^H), and hydrogen–bond basicity (β_2^H). Experiments can be conducted *either at zero relative humidity* (RH) or at some fixed RH, usually 33% or 66%.

Results are analysed by multiple linear regression analysis using equations such as

$$-\log K^H = c + s.\pi_2^* + a.\alpha_2^H + b.\beta_2^H + l.\log L^{16}$$

where L^{16} is the solute Ostwald adsorption coefficient on hexadecane. In this way, any selectivity of the adsorbent towards classes of compound can be investigated. The effect of RH on both activated charcoals and synthetic polymer adsorbents will be discussed, both with respect to the influence of RH on selectivity and on the adsorptivity of the solids.

P23 Equilibria and Excess Thermodynamic Properties of Water–Alkylhydrazines Binary Systems. Application of Test Data for Determination of Association Complex Parameters.

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Abstract has not been received.

P24 The Influence of Hydrogen Bond on the Synergistic Effect of the Solubility of Solids in Binary Solvent Mixtures

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The present work is the continuation of systematic studies on solid–liquid equilibria in systems composed of a polar solute and polar or non–polar solvents. The investigations concern the solubility of pairs of isostructural model aromatic compounds capable of forming intra and intermolecular hydrogen bond: 2-acetyl-1-naphthol, 2-benzoil-1-naphthol and 1-acetyl-2-naphthol, 1-benzoil-2-naphthol in hydrocarbon + alcohol mixtures and are performed in order to confirm the observations made previously. It has been found that solutes, which form the stable intramolecular hydrogen bond, its structural nonpolar analogues, as well as solutes existing in the form of dimers in solution exhibit synergistic effects of solubility (the enhancement of solubility in mixed solvents) in the following systems: hydrocarbons + alcohols, halohydrocarbons + alcohols and cyclohexane + methylene iodide.

On the other hand, when the solutes form the intermolecular hydrogen bond with solvent, the synergistic effects appear in alcohol + ester binary solvents. There was no such an effect in any other binary solvents: ketone + alcohol, water + alcohol, ester + ketone, ester + ether.

P25 The Use of Solubility Diagrams for Solving Crystallochemical Problems

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The solubility of a substance is determined by the energy balance between the bonding factors in the crystal phase and in the solution. For this reason the solubility diagram of an appropriate ternary system of the salt–salt–solvent type can aid the solving structural problems.

Formation of continuous series of mixed crystals. The solubility diagram represents a continuous curve – both salts are isomorphous and this can be used for prediction of the crystal structure type. For example, the structural units in $ZnBr_2.2H_2O$ were predicted from a study of the $ZnBr_2.2H_2O$ – $MgBr_2.2ZnBr_2.6H_2O$ – H_2O system.

Formation of discontinuous series of mixed crystals. The solubility diagram shows a break corresponding to the composition of the solution at which the interruption in the mixed crystal series appears. The free energy of the phase transition from one to the other crystal structure can be estimated using the values of the distribution coefficients of the components between each of the crystal phases and the solution. The isodimorphism in mixed crystal formation offers possibilities for prediction of molecular structures. For example, based on the data of the $Zn(OOCCH_3)_2$ – $Pb(OOCCH_3)_2$ – H_2O system, bidentate–chelate bonded acetates with the Pb^{2+}–ions were expected.

Eutonic type systems are an indication for the absence in both crystal phases of structural units capable of mutual replacement.

The appearance of double salt crystallization fields is an indication for the formation of structural units different from these in both simple salts. A system of rules was developed allowing the prediction of systems in which the double salt formation is expected.

P26 Aqueous solutions of N–methyl morpholin N–oxide. Ultrasonic study

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The aqueous solutions of tertiary amines are good solvents of polysaccharides and also of cellulose. Among these, derivatives of morpholin have been widely studied.

The ultrasonic study performed in our group on N–methyl morpholin N–oxide (NMMNO) solutions has shown some features:

1) An excess absorption is observed in all the investigated solutions (0.2 – 26.5 m)
2) The relaxation frequency is comprised in the measurable frequency range (1–300 MHz) for molality higher than 10 mol kg^{-1}
3) The relaxation frequency increases with increasing water concentration and may be expressed by the following equation

$$\tau^{-1} = (k_{12} + k_{21})C_{water} - \text{Constant}$$

The trend of τ^{-1} may be explained if an equilibrium between two states of water is supposed: bulk and solvated water in equilibrium by means of free molecules:

$$H_2O_{bulk} + H_2O_{free} \Leftrightarrow H_2O_{solv} + H_2O_{free}$$

Equilibria involving NMMNO molecules were not observed except for a sharp variation of bulk viscosity at 2m perhaps due to a structure transition.

P27 Use of the Molecular Theory to Determine Thermodynamic Properties and Solubilities of Non–polar Molecules and Electrolytes of Aqueous Solutions

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The group expansions obtained in the collective variable method are applied to calculate the equilibrium thermodynamic properties of soft sphere ion–dipole mixtures over a wide range of state parameters. The non–electrostatic contribution is determined on the basis of high temperature approximation whereas the electrostatic one is determined on the basis of the ion–dipole model in random phase approximation.

Analytical expressions for the thermodynamic functions are given.

The comparison of the theoretically predicted and experimental values of thermodynamic properties and solubilities for non–polar species and ion aqueous solutions in a wide range of temperature is reported.

P28 Excess Heat Capacities and Excess Volumes of Normal Alkane Mixtures

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We have determined experimentally the excess heat capacities through the composition range at 25, 40, 55 and 70°C for the following binary mixtures of normal alkanes: $C_7 + C_9$, $C_7 + C_{11}$ and $C_7 + C_{13}$. Further the mixture $C_7 + C_{15}$ was studied at 25°C and the mixture $C_7 + C_{20}$ at 40, 55 and 70°C. The excess volume was also measured for the same mixtures and in the same temperature range as above. The C_p^E values are all negative, decreasing in magnitude with increasing T, although for some mixtures the magnitude of C_p^E increases at high values of T. The V^E values also are all negative increasing in magnitude with increasing T for a given mixture and with the difference in chain-length for a given T.

All the C_p^E and V^E results obey the well known Bronsted Principle of Congruence. An extended Corresponding States Principle for chain molecules gives excellent prediction of the temperature and composition dependences of both C_p^E and V^E.